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# Communication—Perovskite Electrochemical System for Highly Selective NO<sub>x</sub> Reduction of Diesel Engine Exhaust

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A perovskite electrochemical system was developed for selective NO<sub>x</sub> reduction of diesel engine exhaust. The system was composed of a La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3±δ</sub> oxidation catalyst and a (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.95</sub>MnO<sub>3±δ</sub>/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> electrochemical cell with BaO nanoparticles. A selectivity of 25–35% was achieved with a NO<sub>x</sub> conversion of 65–75% in 1000 ppm NO with 8% O<sub>2</sub> at 375°C. The superior performance of the system was suggested to be ascribed to the promotion in NO<sub>2</sub> formation substantially activating the NO<sub>x</sub> trapping and reduction processes on the electrode.

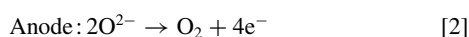
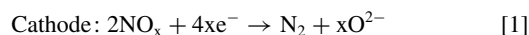
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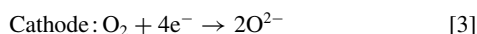
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Nitrogen oxides (NO<sub>x</sub>, NO + NO<sub>2</sub>) are dangerous for both human beings and the environment, causing health problems, acid rain and photochemical smog.<sup>1</sup> The NO<sub>x</sub> removal technology is therefore in high demand, especially in the case of diesel engine exhaust, where excessive oxygen (5–15%) making the reduction of NO<sub>x</sub> (200–1500 ppm) extremely difficult. The mature technologies for NO<sub>x</sub> removal under oxygen-rich conditions require a reducing agent, either from extra fuel or supply of urea/ammonia, which greatly added the system complexity and raised concerns on spill management and secondary pollution.<sup>2</sup>

One attractive technology under development is electrochemical NO<sub>x</sub> reduction, where NO<sub>x</sub> was decomposed to N<sub>2</sub> and O<sub>2</sub> by electron supplied to a solid oxide cell (SOC) (Eqs. 1 and 2). This technology eliminates the need for the addition of reducing materials and shows the potential to be a simpler and advantageous method compared to the commercial ones.<sup>3</sup>



A high selectivity towards NO<sub>x</sub> decomposition (deNO<sub>x</sub>) is crucial for electrochemical NO<sub>x</sub> reduction in order to suppress the competitive reaction of O<sub>2</sub> (Eq. 3).



To achieve satisfactory deNO<sub>x</sub> selectivity, noble metals have been used extensively as electrode materials because of their excellent catalytic activity. However, the noble metal electrodes suffer from issues such as high cost and poor thermal durability. With respect to noble-metal-free deNO<sub>x</sub> cell, Huang et al. adopted the structure and composition of solid oxide fuel cells and achieved an effective NO<sub>x</sub> reduction in the NO<sub>x</sub> concentration higher than 1500 ppm, but the performance declined significantly in the NO<sub>x</sub> concentration of 400 to 1500 ppm<sup>4</sup>. Our previous studies showed the possibility of using perovskite oxide for NO<sub>x</sub> reduction, but the selectivity (<11%) needed to be improved under oxygen-rich conditions.<sup>5,6</sup> For most of the non-precious-metal electrodes (e.g., Ni,<sup>7</sup> Ir,<sup>8</sup> and doped-LaCoO<sub>3</sub><sup>9</sup> etc.), the deNO<sub>x</sub> selectivity was limited to a few percent. Consequently, there is substantial interest in the development of high selective, low-cost, and more durable electrochemical deNO<sub>x</sub> system.

In this study, we report an electrochemical deNO<sub>x</sub> system that is based on perovskite oxides and achieves a highly selective NO<sub>x</sub> reduction in the presence of excess oxygen. This electrochemical system

was composed of a La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3±δ</sub> (LSC) oxidation catalyst and a BaO infiltrated (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.95</sub>MnO<sub>3±δ</sub> (LSM)/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (CGO) electrochemical cell (Fig. 1). LSM is one of the most widely used electrode materials for solid oxide cells, due to its strong catalytic activity, high stability and good economy. The oxidation catalyst was chosen as LSC instead of commonly used Pt catalyst for its comparable performance and better economy. Different from the conventional electrochemical deNO<sub>x</sub>, the working principle of this electrochemical system is to first convert NO to NO<sub>2</sub> by the LSC oxidation catalyst, and subsequently reduce NO<sub>2</sub> to N<sub>2</sub> on the BaO impregnated LSM/CGO cell.

## Experimental or Theoretical

The oxidation catalyst contains 2 wt% La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3±δ</sub> washcoat on a cordierite monolith. The blank cell was fabricated by screen printing a (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.95</sub>MnO<sub>3±δ</sub>/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> composite slurry on both sides of a dense Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> tape. The blank cell was then impregnated with BaO nanoparticles.

The cell was connected to a Gamry Reference 600+ potentiostat for electrochemical measurements. The outlet gas composition was monitored throughout the test by chemiluminescence (Thermo Scientific 42i HL), mass spectrometry (Pfeiffer Vacuum Omnistar GSD 301). Besides, the blank cell and the BaO impregnated cell without the LSC catalyst were tested under the same conditions for comparison.

## Results and Discussion

The NO<sub>x</sub> conversion and current efficiency (CE) for the electrochemical system, the BaO impregnated cell and the blank cell were plotted as a function of temperature and voltage in Figs. 2a–2c. The CE is the ratio of the current consumed by NO<sub>x</sub> reduction to the total current, which is the sum of the current for both NO<sub>x</sub> reduction and O<sub>2</sub> reduction. The value of CE depends not only on the activity of NO<sub>x</sub> reduction but also on that of O<sub>2</sub> reduction, which explains the commonly observed difference in the dependences of the CE and NO<sub>x</sub> conversion on the temperature.<sup>3–7</sup> The perovskite electrochemical system was found to be highly active and selective for NO<sub>x</sub> reduction under oxygen rich conditions. A deNO<sub>x</sub> selectivity of 25–35% was achieved with a NO<sub>x</sub> conversion of 65–75% in 1000 ppm NO with the presence of 8% O<sub>2</sub>. In comparison, the blank LSM/CGO cell was almost inactive in the presence of excess oxygen with the maximum NO<sub>x</sub> conversion less than 8%. The BaO impregnation enhanced the NO<sub>x</sub> reduction compared to the blank cell above 325°C, but the selectivity was basically below 10% in the testing range. BaO has been reported as a typical NO<sub>x</sub> trapping materials which was able to selectively

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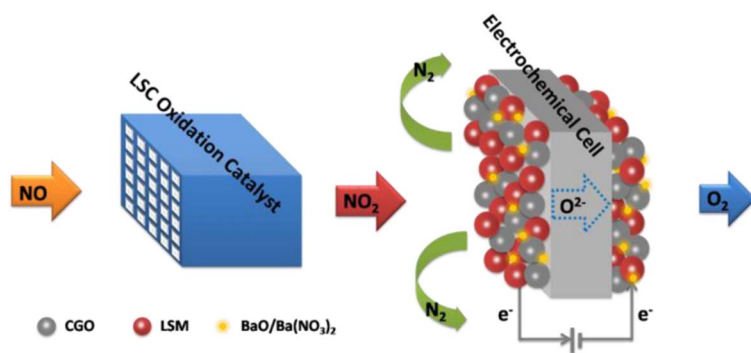


Figure 1. illustration of the principle in the electrochemical system.

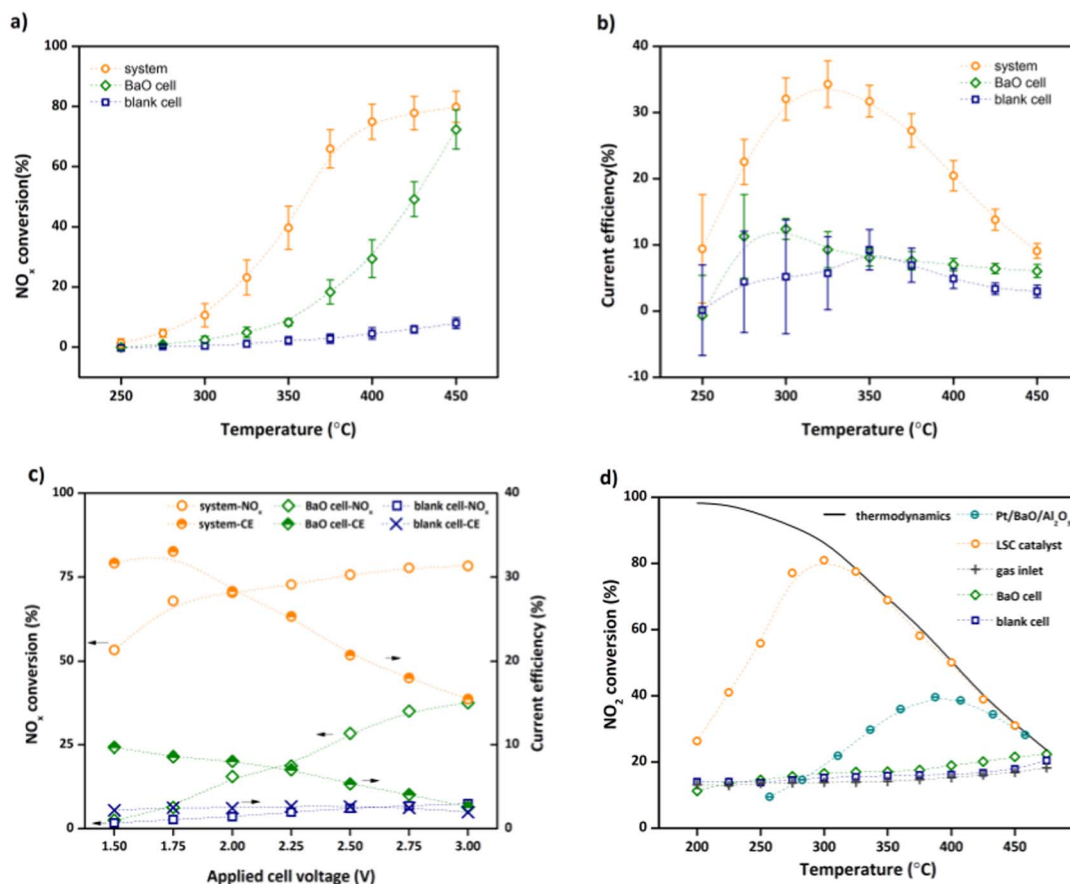
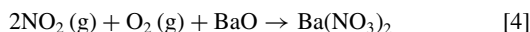


Figure 2. In 1000 ppm NO with 8% O<sub>2</sub>, a) NO<sub>x</sub> conversions and b) current efficiencies as a function of temperature under 2.25 V; c) NO<sub>x</sub> removal properties as a function of voltage at 375°C; d) NO to NO<sub>2</sub> conversion modeled by Factsage and measured in the gas inlet, different cells, LSC and Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>12</sup>

adsorb and store NO<sub>x</sub> species on the electrode surface (Eq. 4).



With respecting to the NO<sub>x</sub> trapping process over BaO, NO<sub>2</sub> has been found to be the sorption precursor or a required intermediate.<sup>2</sup> However, in diesel engines exhaust gases, NO is usually the dominant NO<sub>x</sub> species (~90%). The formation of NO<sub>2</sub> is spontaneous in the oxygen-rich atmosphere due to the thermodynamic equilibrium between NO and NO<sub>2</sub>, whereas this reaction is kinetically limited within a small fraction, especially at low temperatures.<sup>2</sup>

With the LSC catalyst, the NO<sub>2</sub> conversion increased with increasing temperatures within the kinetically limited regime and achieved a maximum of 80% as the equilibrium limit was reached (Fig. 2d). The introduction of LSC catalyst significantly increased the concentration of NO to NO<sub>2</sub> in the gas atmosphere, which could in turn promote the NO<sub>x</sub> trapping process over the BaO sites on the electrodes, especially in the low temperature range.

In addition, the electrode processes of the NO<sub>x</sub> reduction were investigated by Impedance characterization under various temperatures and atmospheres. The spectra at 400°C, at which temperature the system showed both high conversion and selectivity, were listed in Fig. 3 as typical examples. A large arc was observed dominating in the lowest frequency range of spectrum in 1000 ppm NO only. With the presence of oxygen or changing to 1000 ppm NO<sub>2</sub>, this arc disappeared. By fitting the spectra using equivalent circuits established for the LSM cathode,<sup>5,10,11</sup> the summit frequency, activation energy and frequency exponent of the lowest frequency arc were defined as 0.002~0.006 Hz, 0.9~1.1 eV and 0.72~0.8, respectively. The characteristics of this arc fitted well with a conversion arc originated from the lack of the reaction intermediate NO<sub>2</sub> in the NO containing atmospheres.<sup>10,11</sup> This finding suggested that the overall reaction was probably impeded by insufficient NO<sub>2</sub> formation on the LSM electrode. By relieving the limitation of NO<sub>2</sub> formation, the introduction of the LSC catalyst could be able to facilitate the electrochemical NO<sub>x</sub>

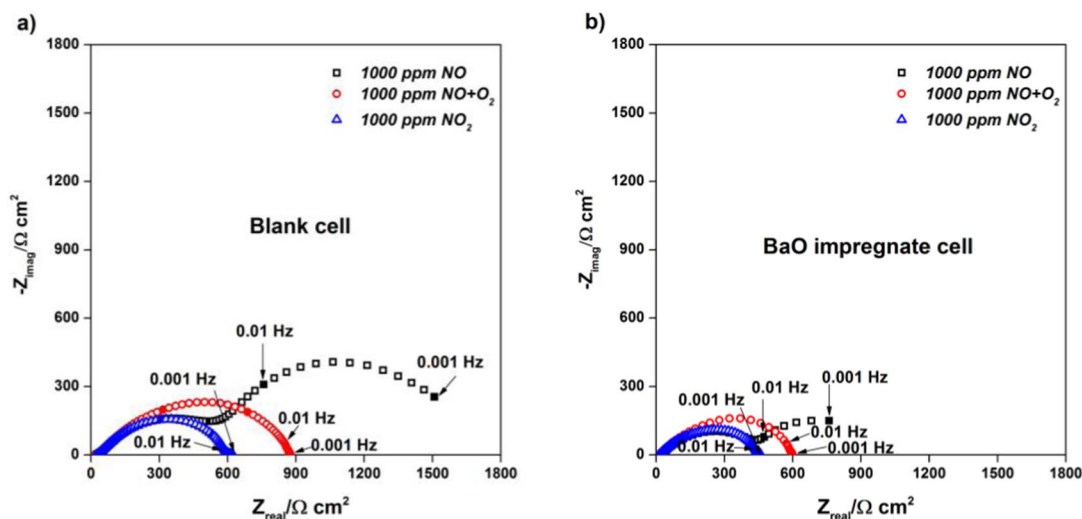


Figure 3. Impedance spectra (Nyquist plot) on the cells in various gas atmospheres at 400°C.

Table I. Results of preliminary durability test on the electrochemical system.

| Properties                              | Simplified gas <sup>a</sup> % | Model gas initial <sup>b</sup> % | Model gas -80h <sup>c</sup> % |
|---|-------------------------------|----------------------------------|-------------------------------|
| NO <sub>x</sub> Conversion              | 67.70                         | 61.26(-9.51 <sup>d</sup> )       | 57.53(-6.09 <sup>e</sup> )    |
| C.E.                                    | 29.78                         | 24.84(-16.58 <sup>d</sup> )      | 23.48(-5.47 <sup>e</sup> )    |
| N <sub>2</sub> selectivity <sup>c</sup> | 59.09                         | 63.57(+7.58 <sup>d</sup> )       | 62.07(-2.42 <sup>e</sup> )    |

<sup>a</sup> 1000 ppm NO with 8% O<sub>2</sub>.

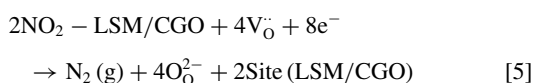
<sup>b</sup> 1000 ppm NO, 8% O<sub>2</sub>, 5% H<sub>2</sub>O, 5% CO<sub>2</sub>.

<sup>c</sup> The N<sub>2</sub> selectivity was calculated as  $2 \times \Delta N_2 / \Delta NO_x$ .

<sup>d</sup> Deviation versus Simplified gas.

<sup>e</sup> Deviation versus Model gas initial.

reduction on the electrode (Eq. 5).



We should point out the difference between the integration of an upstream LSC oxidation catalyst and co-infiltrating the LSC into the electrode with BaO. The co-infiltration was expected to deteriorate the oxidation ability of the LSC due to the loss in dispersion and the steric hindrance by nitrate formation, similar as in the case of Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst<sup>12</sup> shown in Fig. 2d.

Finally, a preliminary durability test of the electrochemical system was performed by operating the system in a model gas of diesel engine exhaust consisting of 1000 ppm NO, 8% O<sub>2</sub>, 5% H<sub>2</sub>O, 5% CO<sub>2</sub> balanced by Ar for approximately 80 hours (Table I). During this period, the system experienced multiple gas changes, voltage variations and two heating cycles from room temperature to 500°C. The switch from the simplified gas to the model gas resulted in a 9.51% decline in the activity and a 16.58% decline in selectivity, which is apparently associated with the coexistence of H<sub>2</sub>O and CO<sub>2</sub>. This was reported to have a positive effect on the electrochemical cell<sup>13</sup> but a harmful effect on the NO<sub>x</sub> adsorption materials and NO oxidation catalyst.<sup>2</sup> Only minor degradation was found after 80 hour operation in the model gas, indicating a satisfying durability of the system regarding the operation time. We presume it is related to the good stability of ceramic structure used in the system. Besides, both the gas atmosphere and operation time showed no evident impact on the N<sub>2</sub> selectivity.

## Summary

A perovskite electrochemical DeNO<sub>x</sub> system was developed by combining a La<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3±δ</sub> oxidation catalyst and a BaO infiltrated (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.95</sub>MnO<sub>3±δ</sub>/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> electrochemical cell. Highly selective NO<sub>x</sub> reduction under oxygen rich conditions was realized on this electrochemical system, which simultaneously eliminated the use of precious metals and the addition of reducing agents. The superior performance of the system was ascribed to the integration of the LSC oxidation catalyst with the BaO impregnated cell promoting the NO<sub>2</sub> formation and substantially activating the NO<sub>x</sub> trapping and electrochemical NO<sub>x</sub> reduction.

## Acknowledgments

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